similar condition of affairs in the case of the corresponding oxygen alkylketodihydroquinazolines and in the acylanthranilicnitriles. The solubility, however, diminishes with increasing molecular weight.

All melting-points recorded in this paper were determined with Anschütz short-scale thermometers, standardized by the Reichs-Anstalt, the entire mercury column being immersed in the heating medium.

The work is being continued.

ORGANIC LABORATORY, HAVEMEYER HALL,
    COLUMBIA UNIVERSITY, January 31, 1903.

ACTION OF METALLIC MAGNESIUM UPON AQUEOUS SOLUTIONS[1].

BY LOUIS KAHLENBERG.

IT has long been known that metallic magnesium acts extremely slowly upon distilled water, and that it practically does not act at all upon solutions of the caustic alkalies. In 1899 Tommasi[2] made qualitative investigations of the action of magnesium on aqueous solutions of the following salts: KCl, NH_4Cl, $CaCl_2$, $MgCl_2$, $NaCl$, $LiCl$, $BaCl_2$, $SrCl_2$, $CuCl_2$, $CdCl_2$, $PbCl_2$, $HgCl_2$, $FeCl_3$, $CrCl_3$, $PtCl_4$, $AuCl_3$, $CuSO_4$, $ZnSO_4$, $FeSO_4$, $MnSO_4$. He found that from solutions of sodium, potassium and lithium chloride, magnesium liberates hydrogen more rapidly than from pure water, magnesium hydroxide being formed. Solutions of the chlorides of barium, strontium, and calcium were acted upon but feebly by magnesium, but ammonium chloride solution was attacked at a lively rate. From solutions of the salts of the heavy metals mentioned above, hydrogen was liberated by magnesium, the chloride or sulphate of that metal being formed, and a basic salt or hydroxide of the heavy metal, or the latter in the metallic state, precipitated. No theoretical explanations were attempted. In the same year G. Lemoine[3] called particular attention to the action of magnesium upon aqueous solutions of magnesium salts. He used solutions of the nitrate, chloride, sulphate and acetate of magnesium, but worked especially with the last three salts. From

aqueous solutions of these salts, magnesium liberates hydrogen rapidly and continuously. Using magnesium in form of powder, he found that about 0.4, the calculated amount of hydrogen, was liberated from a magnesium chloride solution when the powder was present in excess, the action being finally checked by the accumulation of the precipitate formed; but up to the maximum, the quantity of hydrogen disengaged was nearly proportional to the amount of magnesium added. After magnesium had acted upon the solutions of the chloride and acetate, these were found to contain but a relatively slight excess of the base. The analytical data show that the precipitates formed were very basic chloride and acetate of magnesium respectively. In the case of the magnesium sulphate the solution was much weaker after the magnesium had acted upon it, a very considerable portion of the salt having been thrown down in combination with the magnesium hydroxide in form of a basic sulphate of magnesium. Lemoine's explanation of the action of magnesium on solutions of magnesium salts is that in these solutions the salts are slightly decomposed into magnesium hydroxide and free acid. This acid acts on the metal, forming hydrogen and a basic salt which breaks up into the normal salt and hydroxide of magnesium; the latter finally drops out of solution and the reaction begins anew. In advancing this explanation it would certainly seem that Lemoine did not give due weight to the fact that the reaction of the solutions of the magnesium salts toward indicators is perfectly neutral at the outset, and that soon after introducing the magnesium it becomes alkaline and remains so, while the liberation of hydrogen continues unabated. There are thus no facts upon which to base the assumption that the salts he used are even slightly decomposed by water into free acid and magnesium hydroxide.

H. Mouraour[1] again directed attention to the fact that magnesium liberates hydrogen readily not only from solutions of its own salts, but from solutions of other salts as well. He found solutions of the carbonate, chloride, oxalate and sulphide of ammonium strongly acted upon; but no action was observed in the case of a solution of ammonium fluoride. Sodium carbonate, acetate and tetraborate solutions were strongly acted upon, as were also solutions of ordinary and chrome alum. On the other hand, the action

[1] *Compt. Rend.*, **130**, 140 (1900).

was feeble on solutions of sodium phosphate, nitrite, thiosulphate, potassium ferrocyanide and the chlorides of barium, calcium and potassium. The work was entirely qualitative in character. Mouraour states that while Lemoine's explanation of the action may hold good in the case of solutions of chloride of magnesium, for instance, for the most of the salts last mentioned it is inadequate. In the case of the ammonium salts, Mouraour ascribes the action to the fact that solutions of these salts dissolve magnesium hydroxide. But he states that in the case of the salts of lead, copper, mercury and cobalt, from which magnesium precipitates the heavy metals and simultaneously liberates hydrogen, we have a secondary action of the magnesium on the water of the solution. He deems it very difficult to explain the phenomena in the cases last mentioned, stating that it is not probable that salts of these heavy metals favor the solubility of magnesia. Mouraour was apparently not aware of the work of Tommasi. As a matter of fact, magnesium hydroxide is not formed at all when solutions of the heavy metals named are acted upon by magnesium : the salt of the latter metal forms and remains dissolved, the basic salt or hydroxide of the heavy metal being precipitated. In fact, the cases which Mouraour finds difficult to explain are really most readily explained, for the salts of the heavy metals are indeed slightly decomposed by water, a small quantity of free acid being liberated as the acid reaction of such solutions clearly shows. This acid acts on the magnesium, evolving hydrogen and forming the corresponding magnesium salt, a basic salt or hydroxide of the heavy metal resulting simultaneously.

In presenting to my students the various ideas that have from time to time been entertained by scientific men regarding the nature of solutions, I have always laid considerable stress upon the view that the process of solution depends upon a mutual interaction of solvent and solute, and that solutions are chemical combinations[1] of solvent and solute according to variable proportions. Although this view has of recent years been relegated to the background by many, it certainly has a formidable array of facts to support it ; and such facts have really been accumulating more and more, though the investigations yielding them have been guided to a considerable extent by the analogy between gases and solutions.

[1] Compare Mendelejeff : "Principles of Chemistry," Vol. I; Pickering, on solutions, Watts' "Chemical Dictionary;" Horstmann, Graham-Otto : "Lehrbuch der Physikalischen und Theoretischen Chemie," Vol. II.

If when a substance is dissolved in water chemical combination between that substance and water takes place, the liberation of hydrogen from the solution ought to result with a different degree of readiness than from pure water. With this as the guiding idea, Mr. O. W. Brown and Dr. H. V. Black at my suggestion made some preliminary experiments in this laboratory last summer, comparing the rate with which hydrogen is evolved from various aqueous solutions by the action of magnesium upon them. In the course of these experiments (among which many of the observations of the above named French investigators were confirmed, though at the time their researches had not been looked up) it was found that hydrogen was liberated with different rapidity in the case of each solution tested, and that this rate was different from that observed when pure water was used. To my regret Messrs. Brown and Black were unable to continue these investigations, much as they were inclined to do so. It seemed to me well worth while to follow out somewhat further the work thus begun, and the results obtained in investigating the subject will now be presented.

The metallic magnesium used was of Schuchardt's manufacture. It was carefully tested and was found to be free from carbon, and from alkali and alkaline earth metals. 0.8593 gram of the metal yielded 0.0036 gram of the mixed sesquioxides of iron and aluminum. Other metals were not present in the magnesium. The latter was cut into bars of square cross-section measuring 5 mm. on an edge, and having a length of 57.5 mm., thus presenting a surface of 1200 sq. mm. A large number of such bars was prepared. In each liquid to be tested, such a bar was immersed, its surface being first carefully cleaned with fine emery cloth. The action of the metal upon the liquid was noted and the volume of hydrogen evolved at different times was observed. The experiments were conducted at room temperature which was nearly 20°. The ordinary distilled water of the laboratory was used. The chemicals were either of Kahlbaum's or Schuchardt's manufacture; they were tested as to their purity, special care being taken to see that they were free from traces of heavy metals, and in the case of the salts employed, that they were perfectly neutral. Although only one series of results will be given in each case, each series was checked by at least one additional independent series. In the tables that follow, the first

column indicates the solute employed; the heading of each succeeding column indicates the time that a bar of magnesium acted upon the solution in order to liberate the volume of hydrogen given in that column.

TABLE I.

(Solutions contain 2 gram-mols. per liter, except the mannite and sodium sulphate solutions, which contain 1 gram-mol. per liter.)

Solute.	2.5 hours. cc.	23.5 hours. cc.	47.5 hours. cc.	53 hours. cc.
Distilled water (alone)	0.02	0.10	1.5	1.8
Alcohol	0.10	0.40	7.6	7.8
Glycerin	0.01	0.05	0.5	0.55
Cane-sugar	0.10	0.65	1.0	1.2
Mannite	0.08	0.20	0.4	0.55
Urea	1 2	10.6	29.0	31.0
Sodium chloride	7.4	49.8	(discontinued)[1]	
Sodium sulphate	2.4	9.9	18.0	18.8

In the case of the urea solution, ammonia as well as hydrogen was liberated. When sodium nitrate solution is treated with magnesium, only a slight amount of hydrogen is actually evolved; this is due to the fact that the salt is reduced to nitrite. From a solution of ammonium chloride containing 2 gram-mols per liter, over 50 cc. of gas, consisting of hydrogen and ammonia, were liberated by one of the bars of magnesium in five minutes.

TABLE II.

(Solutions contain 1 gram-mol. per liter.)

Solute.	25 min. cc.	40 min. cc.	50 min. cc.	1 hr. cc.	1 hr., 20 min. cc.	1 hr., 35 min. cc.	2 hrs., 56 min. cc.	4 hrs., 23 min. cc.
$MgCl_2$	13.0	18.5	22.0	24.8	30.5	33.8	(discontinued)	
$MgBr_2$	4.8	7.0	8.5	9.9	13.0	14.8	24.5	33.4
$MgSO_4$	5.9	9.4	11.6	13.75	18.5	21.5	36.4	50.5
$Mg(NO_3)_2$	0.2	0.35	0.4	0.45	0.6	0.65	1.2	1.6

TABLE III.

(Solutions contain 1/10 gram-mol. per liter.)

Solute.	25 min. cc.	35 min. cc.	3 hrs., 31 min. cc.	4 hrs., 5 min. cc.	5 hrs., 32 min. cc.	22 hrs., 34 min. cc.
$MgCl_2$	10.8	14.0	43.1	47.6	(discontinued)	
$MgBr_2$	1.8	2.4	7.9	8.6	10.3	25.0
$MgSO_4$	1.8	2.4	7.9	8.6	10.3	27.0
$Mg(NO_3)_2$	0.2	0.3	1.7	1.8	2.2	3.6

[1] The word "discontinued" when used in the tables means that the experiment was discontinued, not that the hydrogen ceased to be evolved. The experiments in these cases had to be stopped because more gas could not be held in the tube used.

TABLE IV.

(Solutions contain 1/100 gram-mol. per liter.)

Solute.	17 min. cc.	31 min. cc.	45 min. cc.	49 min. cc.	2 hrs., 25 min. cc.	3 hrs., 37 min. cc.	5 hrs., 25 min. cc.	22 hrs., 49 min. cc.
$MgCl_2$....	1.8	3.2	4.7	5.2	12.2	15.6	20.0	43.0
$MgBr_2$ ···	1.4	2.0	2.6	2.8	5.8	7.1	9.6	20.9
$MgSO_4$ ···	1.5	2.4	3.0	3.2	6.8	8.8	11.6	29.6

TABLE V.

(Solutions contain 1 gram-mol. per liter.)

Solute.	17. min. cc.	31 min. cc.	45 min. cc.	49 min. cc.
KCl	11.5	17.5	22.5	24.0
KCl + $MgCl_2$	15.0	23.0	29.4	31.4

TABLE VI.

(Solutions contain 1/10 gram-equivalent per liter.)

Solute.	2 min. cc.	4 min. cc.	6 min. cc.	11 min. cc.	16 min. cc.	28 min. cc.	33 min. cc.	36 min. cc.	46 min. cc.
H_2SO_4	3.2	8.0	12.0	21.0	28.0	37.6	40.4	41.8	45.6

Solute.	1 min. cc.	3 min. cc.	5 min. cc.	7 min. cc.	11 min. cc.	14 min. cc.	24 min. cc.	29 min. cc.	49 min. cc.
HCl··	3.0	8.5	14.0	19.0	27.5	31.4	39.4	43.5	48.8

(Solutions contain 1/100 gram-equivalent per liter.)

Solute.	5 min. cc.	10 min. cc.	17 min. cc.	20 min. cc.	30 min. cc.	40 min. cc.	1 hr., 5 min. cc.	1 hr., 20 min. cc.	3 hrs., 37 min. cc.
H_2SO_4	0.4	1.2	2.0	2.5	3.6	4.6	7.0	8.4	14.3
HCl··	0.4	1.2	2.0	2.5	3.6	4.7	7.0	8.0	11.8

It was found that in normal potassium or sodium hydroxide solutions no measurable amount of hydrogen was evolved in twenty-four hours, the magnesium remaining perfectly bright. Solutions of magnesium nitrate when treated with magnesium yield nitrite and finally ammonia, which accounts for the small amount of hydrogen liberated by this salt as compared with other salts of magnesium. From solutions of magnesium acetate and iodide, magnesium also evolves hydrogen rapidly. A magnesium sulphate solution was treated with a large excess of finely divided magnesium, but no reduction of the salt to sulphite took place. From a solution of crystals of $MgCl_2 + 6H_2O$ in glycerin of 1.27 sp. gr., magnesium evolves hydrogen; the action is much increased upon heating. Anhydrous magnesium chloride (prepared from the double magnesium ammonium chloride) dissolved in glycerin of 1.27 sp. gr. acts slowly on magnesium; this action is greatly increased upon raising the temperature. The glycerin itself acts only very slightly on magnesium even on heating.

From $MgCl_2 + 6H_2O$ melted in its crystal water, magnesium evolves hydrogen readily. A saturated solution of $MgCl_2 + 6H_2O$ in ether does not attack magnesium. From a solution of 1 gram-mol. $MgCl_2 + 6H_2O$ in 99.5 per cent. alcohol a bar of magnesium, of the size above described, evolved 2.5 cc. hydrogen in twenty-three hours and forty-seven minutes, while from 99.5 per cent. alcohol alone a like bar of magnesium liberated 0.9 cc. gas in twenty hours and forty-four minutes. Table I shows that from distilled water there was evolved under like conditions only 0.1 cc. in twenty-three and a half hours.

The results in Table I show that during the first twenty-three and a half hours all the solutions except that of glycerin act more vigorously on magnesium than on water alone. Throughout the experiment the glycerin solution lags behind water. After forty-seven and a half hours, more gas has been evolved from the water than from the solutions of glycerin, sugar and mannite, and the same holds true after fifty-three hours. It is especially interesting to note that the alcohol solution is much more vigorous in its action on magnesium than is pure water. The urea solution is relatively vigorously attacked, though, as has been stated, ammonia is also formed in this case. Again, sodium chloride solution is much more vigorous in its action than sodium sulphate solution of equivalent strength.

Tables II, III, and IV show that magnesium evolves hydrogen from solutions of magnesium salts at a fairly rapid rate. The solutions of the magnesium chloride are the most vigorously attacked in all cases. In the solutions containing 1 gram-mol per liter (Table II) the sulphate solution is acted upon more vigorously than that of the bromide; in the solutions containing 0.1 gram-mol per liter (Table III) hydrogen is evolved from the bromide and sulphate solutions at an equal rate for about five hours, within the limits of experimental error, while in the solutions containing 0.01 gram-mol per liter (Table IV) hydrogen is again evolved more rapidly from the sulphate solution than from that of the bromide. In the solution of nitrate of magnesium, nitrite is formed, as mentioned above, which accounts for the fact that but little gas appears in the case of this salt. Table V shows that the potassium chloride solution containing 1 gram-mol per liter acts fully as vigorously as a magnesium chloride solution of 1 gram-mol per liter. The double potassium magnesium chloride

acts still more strongly, as the table indicates. The observation that potassium chloride solutions act readily on magnesium agrees with that of Tommasi; Mouraour called the action feeble.

At my request, Mr. W. R. Mott measured the so-called single differences of potential between magnesium and some of the salt solutions in question. The measurements were made against the normal calomel electrode, the potential of which was taken to be —0.56 volt. He found that at 20° C. the single potential between magnesium and sodium chloride solution (2 gram-mols per liter) is +1.163 volts; between magnesium and sodium hydroxide (1 gram-mol per liter) +1.111 volts, between magnesium and potassium hydroxide (1 gram-mol per liter) +1.140 volts; between magnesium and potassium hydroxide (0.1 gram-mol per liter) 1.105 volts; and between magnesium and magnesium sulphate (1 gram-mol per liter) +1.366 volts. Each result represents the average of four determinations in which different bars of magnesium were used. In the sodium chloride solution, the electromotive force changes but slightly with the time; in the caustic alkali solutions, the electromotive force tends to fall with lapse of time, while in the magnesium sulphate solution the electromotive force increases on standing.

The explanation of the above-described phenomena of the action of metallic magnesium upon aqueous solutions will now be considered. In the case of the saline solutions, one might feel inclined to assume that the salt acts upon the water liberating a certain amount of free acid which attacks the magnesium, resulting in the liberation of hydrogen and the formation of a normal or basic salt or hydroxide of magnesium, according to the nature of the solution under treatment.[1] This would be an attempt to extend Lemoine's interpretation of the action of magnesium upon aqueous solutions of its salts to all aqueous saline solutions. As stated above, there is ground for this explanation in the case of salts of the heavy metals, whose aqueous solutions, as is well known, have acid reactions indicating that they are indeed slightly decomposed by water yielding free acid. But in the case of salts

[1] In the language of the dissociation theory, preferred by some, it would mean that in saline aqueous solutions from which magnesium liberates hydrogen more readily than from pure water, the salt reacts upon the water slightly liberating some free acid, which in turn is electrolytically dissociated, yielding free hydrogen ions. The concentration of hydrogen ions in such solutions would then be greater than in pure water (which is supposed to be only slightly electrolytically dissociated) and this would account for the more vigorous action of magnesium upon saline solutions.

of Mg, Ca, Ba, Sr, K, Na, Li, there is no experimental evidence upon which to base the assumption that in their aqueous solutions there is any free acid present.   Moreover an alkaline reaction is imparted to the solutions of these salts by the magnesium soon after it has been immersed in them, and yet this alkalinity does not interfere with the evolution of hydrogen.[1]

There are no facts upon which to base the assumption that magnesium chloride in aqueous solution suffers greater hydrolytic decomposition (of which free hydrochloric acid is one of the products) than do the chlorides of calcium, barium and strontium for instance; and yet solutions of the last three salts are acted upon but feebly by magnesium, while from the magnesium chloride solution hydrogen is rapidly evolved.   This point is illustrated still more strikingly by the fact that solutions of sodium and potassium chlorides are relatively strongly attacked by magnesium; what reasons are there to assume that these salts are decomposed more by water than those of the alkaline earth metals? And again, would it be rational to suppose that because potassium chloride solutions attack magnesium more readily than sodium chloride solutions, the former salt is decomposed more by water than the latter?   But the difficulty of this mode of explanation becomes even greater in the case of the non-saline solutions.   So for instance the alcoholic solution is acted upon more vigorously than pure water; clearly there is no chance for assuming free acid to be the active agent in the case of this solution.[2]

The idea that Mouraour advances in the case of solutions of ammonium salts, namely, that the solubility of magnesium hydroxide in them determines the liberation of hydrogen from them by action of magnesium, might possibly be applied to other solutions and so the attempt be made to generalize this explanation. In addition to the ammonium salts, there are several cases that might be considered to favor this view.   So magnesium hydroxide is less soluble in solutions of sodium and potassium hydroxide

[1] According to the dissociation theory, such an alkaline solution would contain fewer hydrogen ions than pure water, and yet hydrogen is evolved faster from them than from water.

[2] Indeed from the standpoint of the dissociation theory one would have to hold that the alcohol solution contains fewer hydrogen ions than are present in pure water, and hence action ought to be less than in the latter.   Moreover from the point of view of this theory, magnesium ought to act rather less on solutions of magnesium salts, for the presence of magnesium ions would militate against the formation of more of them.   And again, the difference of potential between magnesium and a magnesium sulphate solution ought to be less than between magnesium and a sodium chloride solution ; the facts show that just the opposite is true.

than in pure water, and the fact that these solutions do not attack the metal as much as does water might be regarded as a support for the view advanced. Again, since ammonium fluoride solution is not acted upon by magnesium, and since the hydroxide and the fluoride of magnesium are insoluble in a solution of ammonium fluoride, this might be urged as another striking instance of the same kind. It would, however, be a delusion to think that the insolubility of magnesium hydroxide in these solutions is what prevents the magnesium from acting upon them. This becomes evident from the following experiment. On making magnesium amalgam (by heating magnesium and mercury together) and treating normal solutions of potassium and sodium hydroxide with the same, I found that hydrogen is very rapidly evolved, magnesium hydroxide formed, and mercury set free from the amalgam. Solution of ammonium fluoride is also violently attacked by magnesium amalgam with the concomitant liberation of hydrogen. Mere contact of magnesium and mercury in these solutions will not bring about this action, the amalgam must be used.

At a given temperature and pressure the course that a chemical reaction will take is determined (1) by the chemical affinity between the reacting substances and (2) by the relative masses of these substances. If the system consists of a solid immersed in a liquid, the rate of action depends on the amount of surface of the solid exposed to the liquid. If the product is an insoluble one and closely envelops the surface of the solid that is being acted upon, the rate of the action will be diminished because of diminution of the surface exposed. This effect of the accumulation of the insoluble product of the reaction increases, the longer the reaction goes on, and may finally practically check the process, which is clearly shown by the results of Lemoine cited above. While there can be no doubt of this effect, nevertheless, the differences in the rates of evolution of hydrogen during the times recorded above are in general too great to be accounted for solely on the basis of accumulation of the precipitate. Of this I became especially convinced by treating aqueous solutions with sodium amalgam; in these cases, where no precipitate forms, similar large differences in the rate of evolution of hydrogen occur.[1] Again it is well to

[1] This most interesting problem of the action of alkali metals and their amalgams upon aqueous solutions is being studied in this laboratory by Mr. Gustav Fernekes at present. His work is already well advanced.

bear in mind in this connection, that during the time of duration of the above experiments but small quantities of magnesium hydroxide or basic magnesium salts were formed; in fact, in many cases a precipitate was not at all discernible. I assured myself that from a bar of magnesium that had remained in a normal solution of sodium chloride long enough to be visibly covered with a white coating, hydrogen was nevertheless much more rapidly evolved than from a fresh bar of magnesium just placed in water.

One might further be inclined to ascribe the action of magnesium on these aqueous solutions to mere contact action, i. c., to so-called catalytic action of the solute or some of its ingredients. Tommasi[1] states that in the case of the potassium chloride solution we apparently have the best instance of such contact action, for here the potassium chloride remains unchanged and the magnesium hydroxide only is formed. Nevertheless even here it is not an easy matter to free the latter from "adhering chlorides" by washing. It would scarcely be helpful to dismiss the matter by saying that in these diverse solutions the rate of evolution of hydrogen is increased by the catalytic action of the solute when the hydrogen is liberated more rapidly than from water, and that the rate is diminished by the negative catalytic action of the solute, when the formation of hydrogen takes place less rapidly than from water.

All the facts above presented are very readily explained on the basis of the view of solutions which suggested this research; namely, that solutions are chemical combinations of solvent and solute according to variable proportions.[2] It is clear that if water is chemically bound to the substance dissolved in it, the readiness with which metallic magnesium or sodium amalgam will liberate hydrogen from different solutions will in general be different. Again, the difference of potential between magnesium and the solutions would be expected to be higher in the case of solutions that are vigorously attacked than in solutions in which the action is slight. The experimental data are in accord with this. If the chemical affinity existing between magnesium and the solution (regarded as a chemical combination of solvent with solute) is

[1] Loc. cit.

[2] The view that solutions are chemical combinations according to variable proportions, does not detract one particle from the law of definite proportions which is well established in the case of so very many compounds. Horstmann (loc. cit.) presents the whole matter so well that it is unnecessary to dwell further upon it here.

sufficient to overcome the cohesion of the magnesium, the latter is attacked; from the resulting compound hydrogen splits off, and the rest may all remain as a homogeneous liquid (*i. e.*, all may remain dissolved) or further decomposition into a precipitate, the hydroxide or basic salt, and a solution may occur and usually does occur after the action has progressed for a sufficient time. If no precipitate forms, the rate of change is not diminished by a decrease of the surface of metal exposed, and so the reaction is apparently aided. The more readily the dissolved products are removed from proximity of the surface of the metal by diffusion aided by mechanical stirring of some kind, the more rapidly the change progresses. Usually, as the gas is rapidly evolved, the liquid receives considerable stirring from this source. If the specific attraction called chemical affinity existing between magnesium and the solution is not sufficient at the temperature of experiment, to overcome the cohesion of the magnesium, no action will take place as in normal potassium hydroxide solution for instance; if the affinity is barely able to overcome the cohesion, the action will go on very slowly, as in the case of water. As stated above, magnesium amalgam does act on normal potassium hydroxide solution with vigor, liberating hydrogen, forming magnesium hydroxide and setting mercury free. The explanation of the action is similar to the one just given. Here the affinity between the solution and the amalgam is sufficient to disintegrate the latter, and magnesium hydroxide forms in spite of the fact that it is difficultly soluble. Under the conditions of the experiment, it is evidently easier to abstract magnesium from magnesium amalgam than to overcome· the cohesion of pure magnesium. This is in harmony with the fact that magnesium amalgam does not form when magnesium and mercury are brought together at ordinary temperatures;[1] it requires a higher temperature in order that the union of the metals will take place.

The view that solutions are chemical combinations of solvent and solute may seem somewhat antiquated at the present time when purely physical conceptions of solutions are in predominance. But this older view is still held by eminent chemists and physicists, for it gives an adequate cause for the process of solution, for the thermal changes accompanying the latter, and for the

[1] At ordinary temperatures the affinity between these metals is not able to overcome their cohesions. Compare the work of Wanklyn and Chapman on magnesium amalgam in the *J. Chem. Soc.* [London], (2), **4**, 141.

fact that (exclusive of the mass) the properties of a solution are never found to be quite equal to the sum of the properties of solvent and solute. Moreover, facts known at present concerning both dilute and concentrated solutions are entirely compatible with it, and it will no doubt prove a most valuable aid in further research.

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THE VOLUMETRIC DETERMINATION OF MANGANESE IN IRON AND STEEL.

BY HARRY E. WALTERS.

IN a recent number of this Journal, **24,** 1206 (1902), there appeared an article by Stehman entitled "The Determination of Manganese in Iron and Steel" in which the author stated that in attempting to replace lead peroxide with ammonium persulphate and titrating with sodium arsenite, the silver salt, of course, caused trouble. If, however, the silver salt is thrown out of solution before the titration is begun, as insoluble silver chloride, the determination of the permanganic acid by a standard solution of sodium arsenite may be readily accomplished.

With the exception of the titration, the method is the same as that proposed by me in September, 1901.[1] While preparing that method the writer also tried to make a titration method but without success, as the hot solutions were titrated and the reaction between the excess of persulphate and the silver nitrate caused the results to be high and irregular.

Since the article by Stehman appeared, I have doubted the necessity of precipitating the silver as chloride, if the solution be cooled before the titration is begun. In order to prove the correctness of this view a number of samples were taken and treated as follows: 0.2 gram of the samples and a standard steel of known manganese content were weighed off into suitable test-tubes or beakers and 10 cc. of nitric acid (sp. gr. 1.20) were added to each. The solutions were heated until the samples were dissolved and all nitrous fumes driven off. Fifteen cc. of a solution of silver nitrate equal to 0.02 gram silver nitrate (1.33 grams of the salt to

[1] This Journal, **24,** R. 12.